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(54) Reinforced thermoplastic compositions of polyester resins and glass fibres in combination with particulate mica

(57) The invention concerns moulding compositions comprising a poly(1,4-butylene terephthalate) resin, and a poly(ethylene terephthalate) resin, comprising a reinforcing agent which is a combination of glass fibres and particulate mica having a particle size from 325 to 10 mesh (U.S. Standard Sieve), preferably less than 100 mesh. Preferably the reinforcing agent comprises from 1 to 15 parts of glass fibres and 15 to 30 parts of mica, per 100 parts by weight of composition. The presence of the mica leads to enhanced resistance to warpage, and a higher deflection temperature under load.

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SPECIFICATION

Reinforced thermoplastic compositions of polyester resins and glass fibres in combination with particulate mica

This invention relates to glass reinforced moulding compositions which have improved deflection temperature under load and/or warp resistance in the moulded article. More particularly, it pertains to compositions comprising a polyblend of poly(1,4-butylene terephthalate) resin and poly(ethylene terephthalate) resin, and as a reinforcement therefor, glass fibres combined with particulate mica.

High molecular weight linear polyesters and copolyesters of glycols and terephthalic or isophthalic acid have been available for a number of years. These are described *inter alia* in U.S. Patents No. 2,465,319 and 3,047,539 which disclose that the polyesters are particularly advantageous as film and fibre formers.

With the development of molecular weight control, the use of nucleating agents and two-step moulding cycles, poly(ethylene terephthalate) had become an important constituent of injection mouldable compositions. Poly(1,4-butylene terephthalate), because of its very rapid crystallization from the melt, is uniquely useful as a component in such compositions. Workpieces moulded from such polyester resins, in comparison with other thermoplastics, offer a high degree of surface hardness and abrasion resistance, high gloss, and lower surface friction.

It is known that glass reinforced thermoplastic compositions of poly(1,4-butylene terephthalate) and poly(ethylene terephthalate), can be moulded to articles having greater resistance to warpage and/or higher deflection temperature under load (DTUL), if a small, effective amount of talc is included and the amount of glass is maintained below 10 parts by weight per 100 parts by weight of the composition.

Our prior British Patent Application No. 50659/77 discloses thermoplastic moulding compositions which comprise an intimate mixture of:

(a) a poly(1,4-butylene terephthalate) resin;
(b) a poly(ethylene terephthalate) resin; and
(c) a reinforcing agent combination in an amount at least sufficient to provide reinforcement, and comprising (i) glass fibres and (ii) fine particle size ground mica, having a particle size of less than 325 mesh (U.S. Standard Sieve).

We have now discovered that superior polyblends of poly(1,4-butylene terephthalate) resin and poly(ethylene terephthalate) resin, reinforced with fibrous glass, in combination with particulate mica are obtained when the mica has a larger particle size.

The present invention provides a thermoplastic moulding composition which comprises an intimate mixture of

(a) a poly(1,4-butylene terephthalate) resin;
(b) a poly(ethylene terephthalate) resin;
(c) a reinforcing agent combination in an amount at least sufficient to provide reinforcement, and comprising (i) glass fibres and (ii) particulate mica having a particle size of from 325 to 10 mesh (U.S. Standard Sieve).

The prior art does not suggest the present discovery. For example, U.S. Patent No. 3,953,394 shows conventionally reinforced polyblends of poly(1,4-butylene terephthalate) and poly(ethylene terephthalate), and glass, but there is no suggestion that a second filler, mica, can be used to improve resistance to warpage. Moreover, U.S. Patent No. 3,824,209 shows mica, but in polyester combinations wherein the latter must not be fibre-formers, which excludes poly(ethylene terephthalate), and there is no mention that mica is useful to improve warp resistance. Finally, U.S. Patent No. 1,123,985 discloses mica powder with an inorganic binding agent, such as boron-silicon-lead, having a melting point of 500—950°C. Apart from the fact that this invention is concerned with organic resins and mica, there is no suggestion in U.S. Patent No. 1,123,985 which would assist one skilled in this art to improve the resistance to warpage in the compositions of U.S. Patent No. 3,953,394.

The examples to be presented hereinafter demonstrate that the new compositions possess less inherent warpage in the moulded article, and good mouldability, when compared with compositions of glass fibre-reinforced polyblends of polyester resins. The improved DTUL and decrease in warpage is achieved without any appreciable decrease in other mechanical properties such as notched Izod impact strength, tensile strength and modulus. The flexural strength is improved.

The mica suitable for use in accordance with this invention as component (c) (ii), can be obtained from a number of commercial sources.

By "particulate", it is meant that the material will be ground or otherwise sized or comminuted to a particle size from 325 to 10 mesh, (U.S. Standard Sieve). Suitable commercial micas are available, e.g., from Martin-Marietta under the tradename Suzorite (20 H, 10—20 mesh; 200 H, less than 100 mesh; 200 S, less than 100 mesh; 80 S, 99% less than 100 mesh), and from the English Mica Co.,

Stamford Connecticut 06905 under the tradename C—1000 (water ground, less than 325 mesh). The best combination of properties, including warp, impact, overall strength and paintability appears to be conferred by a mica typically represented by Suzorite 200 S.

The polyester resins of the compositions of this invention are available commercially or can be prepared by known techniques, such as by the alcoholysis of esters of terephthalic acid with ethylene glycol or 1,4-butanediol, and subsequent polymerization, by heating the glycols with the free acids or with halide derivatives thereof, and similar processes. These are described, for example, in U.S. Patents No. 2,465,319; 3,047,539.

Illustratively, these high molecular weight polyesters will have an intrinsic viscosity of at least 0.4 deciliters/gram, and preferably at least 0.5 deciliters/gram, as measured in a 60:40 phenol/tetrachloroethane mixture at 30°C.

In preferred embodiments component (a) comprises from 1 to 99 parts by weight, and component (b) comprises from 99 to 1 parts by weight, per 100 parts by weight of the total resinous components in the composition.

The filamentous glass to be employed as component (c) (i) of the reinforcement in the present compositions is well known to those skilled in the art, and is widely available from a number of manufacturers. For compositions ultimately to be employed for electrical uses, it is preferred to use fibrous glass filaments comprised of lime-aluminum borosilicate glass that is relatively soda free. This is known as "E" glass. However, other glasses are useful where electrical properties are not so important, e.g., the low soda glass known as "C" glass. The filaments are made by standard processes, e.g., by steam or air blowing, flame blowing and mechanical pulling. The preferred filaments for plastics reinforcement are made by mechanical pulling. The filament diameters may range from 0.00003 to 0.002 cm., but this is not critical to the present invention.

The length of the glass filaments, and whether or not they are bundled into fibres and the fibres bundled in turn to yarns, ropes or rovings, or woven into mats, are also not critical to the invention. However, in preparing the moulding compositions, it is convenient to use the filamentous glass in the form of chopped strands of from 0.3 to 5 cm., long. In articles moulded from the compositions, on the other hand, even shorter lengths will be encountered because, during compounding, considerable fragmentation will occur. This is desirable, however, because the best properties are exhibited by thermoplastic injection moulded articles in which the filament lengths lie between 0.00025 and 0.3 cm.

In general, best properties will be obtained if the reinforcing agent combination comprises at least 1 part by weight, and, preferably, from 1 to 60 parts by weight, based on 100 parts of the combined weights of components (a), (b) and (c).

In the most preferred compositions, the glass fibres (c) (i) comprise from 1 to 15 parts by weight, and the mica component (c) (ii) comprises from 15 to 30 parts by weight, per 100 parts by weight of components (a), (b) and (c).

The compositions of this invention can include, in addition to the reinforcement combination, other ingredients, such as dyes, pigments, stabilizers, plasticizers, flame retardants and drip retardants, added for their conventionally employed purposes. Illustrative flame retardant additives are disclosed in U.S. Patents No. 3,833,685; 3,915,926; 3,671,487; 3,681,281; 3,557,053 and 3,830,771 and British Patent No. 1,358,080.

The compositions of this invention can be prepared by a number of procedures. In one procedure, the reinforcement, e.g., glass fibres and mica, is put into an extrusion compounder with the resinous components to produce moulding pellets. The reinforcement is dispersed in a matrix of the resin in the process. In another procedure, the reinforcement combination (c) is mixed with the resins (a) and (b) by dry blending, then either fluxed on a mill and comminuted, or they are extruded and chopped. The reinforcing agent combination can also be mixed with the resins and directly moulded, e.g., by injection or transfer moulding techniques.

Although it is not essential, best results are obtained if the ingredients are pre-compounded, pelletized and then moulded. Pre-compounding can be carried out in conventional equipment. For example, after carefully pre-drying the polyester and the reinforcing agent combination, e.g., at 125°C. for 4 hours, a single screw extruder is fed with a dry blend of the ingredients, the screw employed having long transition and metering sections to ensure proper melting. On the other hand, a twin screw extrusion machine, e.g., a Werner & Pfleiderer machine can be fed with resins and additives at the feed port and reinforcement down stream. In either case, a generally suitable machine temperature will be 230 to 300°C.

The pre-compounded composition can be extruded and cut up into a suitable form, such as conventional granules, or pellets, by standard techniques.

The compositions can be moulded in any equipment conventionally used for glass-filled thermoplastic compositions, e.g., a Newbury type injection moulding machine with conventional cylinder temperatures, e.g., 275°C. and conventional mould temperatures, e.g., 65°C.

EXAMPLES 1 TO 3.

A dry blend of poly(1,4-butylene terephthalate), intrinsic viscosity 0.8 dl/g, melt viscosity 1700 poise at 250°C, poly(ethylene terephthalate), intrinsic viscosity 0.62 dl/g., 0.3 cm (1/8 inch) glass fibres

(Owens Corning P. 419), particulate mica, Ferro 904 antioxidant are compounded and extruded at 275°C (525°F) in an extruder. The extrudate is pelletized and injection moulded at 275°C (525°F), moulding temperature 55°C (130°F). The formulations and physical properties obtained are shown in Table 1:

Table 1 — Compositions of Polyester Resins, Glass and Mica

Example	1	2	3
Ingredients (parts by weight)			
poly(1,4-butylene terephthalate)	46.7	41.7	31.7
poly(ethylene terephthalate)	5	10	15
fibrous glass reinforcement	11	11	11
mica, 10—20 mesh[a]	25	25	25
antioxidant[b]	.05/1.5	.05/1.5	.05/1.5
impact modifier[c]	10	10	10
polyethylene[d]	2	2	2
mould release[e]	0.1	0.1	0.1
Properties			
Deflection Temperature (°C) under load at 185618 Kg. m^{-2}	180	177	160
Warp: as moulded, mm.	0	0	<1
after 30 min. at 176°C mm.	<1	1	<1
Notched Izod impact $J.m^{-1}$	69.4	69.4	58.7
Unnotched Izod impact $J.m^{-1}$	234.9	234.9	234.9
Tensile strength, $Kg.m^{-2}$	5.7×10^6	5.9×10^6	5.55×10^6

a Suzorite 20 H
b Ferro 904/Irganox 1093
c Copel 3320 — Silicone — polycarbonate block copolymer (GE)
d Microthene FN 510 (U.S.I. Chemicals)
e Mold Wiz (Int. EQ—6)

The resistance to warpage is remarkable.

EXAMPLES 4 TO 8.

Following the general procedure of Examples 1 to 3 a series of formulations according to this invention are prepared moulded and tested. The antioxidant, polyethylene and mould release are identified in Table 1. The results are set forth in Table 2.

Table 2 — Composition of Polyester Resins, Glass and Mica

Example	4	5	6	7	8
Composition (parts by weight)					
poly(1,4-butylene terephthalate)	41.7	36.7	31.7	31.7	28.7
poly(ethylene terephthalate)	10	15	20	20	20
fibrous glass	11	11	11	11	11
mica, 10—20 mesh[a]	25	25	25	—	25
mica, 99% <100 mesh[b]	—	—	—	25	—
antioxidant	.05/.15	.05/.15	.05/.15	.05/.15	.05/.15
impact modifier[c]	10	10	10	10	—
impact modifier[d]	—	—	—	—	15
polyethylene	2	2	2	2	—
mould release	0.1	0.1	0.1	0.1	0.1
Properties					
Deflection Temperature (°C) under load at 185618 $Kg.m^{-2}$	178	182	177	188	154
Warp: as moulded, mm.	0	0	0	2	0
after 30 min. at 176°C., mm.	0	<1	<1	2.8	<1
Notched Izod impact, $J.m^{-1}$	64.0	58.7	64.0	48.0	74.7
Unnotched Izod impact, $J.m^{-1}$	208.2	202.8	229.5	331.0	234.9

a Suzorite 20 H
b Suzorite 80 S
c Copel 3320 (see Table 1)
d Hytrel 4056, Dupont, segmented copolyester.

The compositions have excellent resistance to warpage.

EXAMPLES 9 TO 12.

The general procedure of Examples 1 to 3 is repeated and a series of formulations according to this invention is prepared, moulded and tested. The results are set forth in Table 3.

Table 3 — Compositions of Polyester Resins Glass and Mica

Example	9	10	11	12
Compositions (parts by weight)				
poly(1,4-butylene terephthalate)	31.7	28.7	31.7	28.7
poly(ethylene terephthalate)	20	20	20	20
fibrous glass	11	11	11	11
mica, 10—20 mesh[a]	—	25	25	—
mica, <100 mesh[b]	25	—	—	—
mica, 99% <100 mesh[c]	—	—	—	25
antioxidant*	.05/.15	.05/.15	.05/.15	.05/.15
impact modifier[d]	—	15	10	15
impact modifier[e]	10	—	—	—
polyethylene*	2	—	2	—
mould release*	0.1	0.1	0.1	0.1
Properties				
Deflection Temperature (°C) under load at 185618 Kg.m^{-2}	182	152	165	161
Warp: as moulded, mm.	1.5	0	0	1.5
after 30 min. at 176°C mm.	7	2.5	1	8
Notched Izod impact, J.m^{-1}	53.4	74.7	64.0	53.4
Unnotched Izod impact, J.m^{-1}	368.3	250.9	256.2	384.3
Flexural strength, Kg.m^{-2}	1.11×10^7	—	—	—
Flexural, modulus, Kg.m^{-2}	5.9×10^8	—	—	—
Tensile strength, Kg.m^{-2}	6.6×10^6	—	—	—

a Suzorite 20 H
b Suzorite 200 S
c Suzorite 80 S
d Hytrel 4056, Dupont
e Rohm & Haas, XP7709

* See Table 1

EXAMPLES 13 AND 14.

Because the mica designated Suzorite 200 S appears to confer the best balance of overall properties, e.g., warp, impact, strength and paintability, two additional formulations are prepared, moulded and tested following the general procedure of Examples 1 to 3. The results are set forth in Table 4.

Table 4 — Compositions Comprising Polyester Resins, Glass Fibres and Mica

Example	13	14
Compositions (parts by weight)		
poly(1,4-butylene terephthalate)	31.7	31.7
poly(ethylene terephthalate)	20	20
fibrous glass	11	11
mica, <100 mesh[a]	25	25
antioxidant*	.05/.15	.05/.15
impact modifier[b]	10	—
impact modifier[c]	—	10
polyethylene*	2	2
mould release*	0.1	0.1
Properties		
Deflection Temperature (°C) under load at	174	168
Warp, as moulded, mm.	0	0
after 30 min. at 176°C., mm.	9	9
Notched Izod impact, $J.m^{-1}$	58.7	53.4
Unnotched Izod impact, $J.m^{-1}$	373.7	363.0
Flexural strength	1.2×10^7	1.1×10^7
Flexural modulus	6.10×10^8	5.81×10^8
Tensile strength	7.17×10^6	6.96×10^6

a Suzorite 200 S
b Hytrel 4056
c LR 3320

* See Table 1

CLAIMS

1. A thermoplastic moulding composition which comprises an intimate mixture of

(a) a poly(1,4-butylene terephthalate) resin;
(b) a poly(ethylene terephthalate) resin;
(c) a reinforcing agent combination in an amount at least sufficient to provide reinforcement, and comprising (i) glass fibres and (ii) particulate mica having a particle size of from 325 to 10 mesh (U.S. Standard Sieve).

2. A composition as claimed in Claim 1 wherein the mica has a particle size of less than 100 mesh.

3. A composition as claimed in Claim 1 or 2 wherein component (a) comprises from 1 to 99 parts by weight and component (b) comprises from 99 to 1 parts by weight, per 100 parts by weight of the total resinous components in the composition.

4. A composition as claimed in any preceding Claim wherein the reinforcing agent combination is present in an amount of at least 1 part by weight per 100 parts by weight of the combined components (a), (b) and (c).

5. A composition as claimed in Claim 4 wherein the reinforcing agent combination is present in an amount of from 1 to 60 parts by weight per 100 parts by weight of the combined components (a), (b) and (c).

6. A composition as claimed in any preceding Claim wherein the glass fibres (c) (i) comprise from 1 to 15 parts by weight and the mica component (c) (ii) comprises from 15 to 30 parts by weight, per 100 parts by weight of components (a), (b) and (c).

7. A composition as claimed in Claim 1 and substantially as hereinbefore described with reference to any of the Examples.

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